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PHOTOSTABILITY OF ACETYLATED WOOD COATED WITH NANO ZINC OXIDE

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ABSTRACT

Chemical modification with acetic anhydride is an effective method to stabilise wood against dimensional movement and improve decay resistance of wood. It has also been reported to retard UV light induced color darkening on wood surface. Coatings of wood surfaces with certain nano metal oxides have also shown promise as UV screening agent. In this work, we have evaluated synergistic effect of acetylation of wood and application of nano material on wood surfaces to enhance their UV stability. Photo-stability of acetylated *Wrightia tinctoria* wood coated with zinc oxide (ZnO) nanodispersion was evaluated by irradiating these wood specimens to UV radiation in an accelerated weathering tester. Acetylation of wood with acetic anhydride exhibited photo-bleaching and inhibited light-induced color darkening observed in unmodified wood. Coating of unmodified and modified wood surfaces with ZnO nanodispersion reduced photo-discolouration and degradation of wood polymers. The photo-bleaching observed in chemically modified wood upon light irradiation was further enhanced by application of nano coating on wood surfaces.

Keywords: Chemical modification, nano material, photodegradation, zinc oxide, wood, *Wrightia tinctorial*.

INTRODUCTION

Wood and wood products exposed outdoors are prone to abiotic and biotic degradation and require protective measures under outdoor applications. All the polymeric components of wood (cellulose, hemicelluloses and lignin) possess free hydroxyl groups, which make wood hydrophilic and results in its dimensional instability due to moisture absorption or desorption. Affinity to moisture also promotes microbial attack. Strong absorption of UV light by wood polymers, particularly lignin, makes wood surfaces susceptible to degradation due to solar radiation. Chromophores in lignin strongly absorb UV radiations and are prone to photochemical degradation. Degradation occurs through a series of free radical initiated chemical reactions resulting in accumulation of carbonyl moieties leading to photo-yellowing of the exposed wood surfaces (Feist and Hon 1984; Hon and Chang 1984; Tolvaj and Faix 1995; Hon 2001; Muller *et al.* 2003; Pandey 2005).

The properties of wood can be upgraded by esterification of hydrophilic hydroxyl groups to make it hydrophobic. The chemical modification enhances biological resistance, reduces moisture adsorption and imparts dimensional stability of wood (Rowell 2005, 2006, 2013; Takahashi 1996; Plakette *et al.* 1996; Matsuda 1996; Giridhar *et al.* 2017). One of the most efficient modification processes is esterification with acetic anhydride (Rowell 2005; Rowell 2013; Rowell 2005; Chang and Chang 2002). It also provides UV resistance and inhibits light induced darkening (yellowing) of wood surfaces and therefore modified wood retains its natural appearance for longer duration (Rowell 2017; Vollmer and Evans 2013; Pandey and Srinivas 2015; Evans *et al.* 2000; Williams 2005; Nagarajappa and Pandey 2016). Chemical modification of wood with acetic anhydride is also effective in decreasing light induced discoloration (Evans *et al.* 2002; Chang and Chang 2001; Pandey and Pittman 2002; Ohkoshi 2002).

Certain inorganic metal oxides (e.g., zinc oxide, titanium dioxide etc.) act as UV stabilizer by absorption or scattering of light. Reduction of the size to nanometer scale further enhances light absorption by these materials due to increased surface area. Coating with these inorganic nanoparticles has been found to induce UV resistance in wood to considerable extent (Clausen *et al.* 2010; Lowry *et al.* 2008; Cristea *et al.* 2010; Sahin and Mantanis 2011; Forsthuber *et al.* 2013; Habibzade *et al.* 2014; Afrouzi *et al.* 2013; Nair *et al.* 2018).

In this work, we had investigated influence of ZnO nanoparticle coating on UV stabilization of chemically modified wood. Wood specimens of *Wrightia tinctoria* were chemically modified with acetic anhydride. Unmodified and acetylated wood surfaces were coated with ZnO nanodispersions in propylene glycol using a sprayer and were irradiated with UV light in a QUV accelerated weathering tester equipped with UVA-340 nm light source. Extent of degradation was analyzed by evaluating color changes (using spectrophotometer) and chemical changes (monitored by using FTIR spectroscopy) on wood surfaces. In an earlier work, we had examined the UV resistance of unmodified wood coated with dispersions of nano metal oxides (ZnO, cerium oxide and titanium oxide) and found that these nano materials were very effective in imparting UV resistance on wood surfaces (Nair *et al.* 2018). However, performance of nanomaterial coating on photo-stabilization of chemically modified wood has not been studied.

MATERIALS AND METHODS

Materials:

Defect free specimens of *Wrightia tinctoria* wood of size 150 mm x 3,5 mm x 5 mm (length x width x thickness) were prepared. Acetic anhydride (99 %, AR grade) was purchased from Pallav Chemicals, Mumbai, India. Zinc oxide (ZnO) nanopowder (particle size < 100 nm) was purchased

from Sigma Aldrich Chemicals Pvt. Ltd., Bengaluru, India. Propylene glycol (PG) and N-bromosuccinimide (NBS) (99,5 %) were purchased from Central Drug House, India.

Nanodispersions of ZnO in PG:

Nanodispersion of ZnO in PG was prepared according to the procedure discussed elsewhere (Nair *et al.* 2018). A stable homogenous solution, without any agglomeration, was obtained by stirring nanoparticle-PG mixture for 10 min in a homogeniser (IKA T25 Digital Ultra-Turrax) followed by sonication in an ultrasonicator (Heischer Ultra sound Technology UP400S). UV-Visible absorption spectroscopy and Scanning Electron Microscopy (SEM) were used to characterise ZnO nanodispersion (Nair *et al.* 2018).

Acetylation of wood:

Specimens of *W. tinctoria* (size 150 mm x 3,5 mm x 5 mm) were acetylated with acetic anhydride using N-bromosuccinimide (NBS) as catalyst (concentration 2 % weight /volume) as per the procedure described by Nagarajappa *et al.* 2015. Reaction was carried out in an oil bath (reaction conditions: temperature - 105 °C, reaction time - 4 h) in a glass vessel connected to a water condenser. The unreacted reagent (acetic anhydride) was removed by extracting modified wood specimens with acetone and toluene (1:1) in a Soxhlet extractor. Weight percent gain (WPG) was estimated from oven dried weight of unmodified (W_0) and chemically modified (W_m) wood using equation (1).

$$WPG = \left[\frac{W_m - W_0}{W_0} \right] \times 100 \quad (1)$$

Evaluation of UV resistance:

Unmodified and acetylated wood specimens coated with ZnO nanodispersions (concentration 1,0 % and 2,0 % weight/volume, two coats). The amount of applied coating on the surface was $0,0008 \text{ g}\cdot\text{cm}^{-2}$ for 2 % dispersion and $0,0004 \text{ g}\cdot\text{cm}^{-2}$ for 1 % dispersion.

UV resistance was evaluated by exposing coated wood (four replicates for each case) in a QUV accelerated weathering tester (Q-Lab, USA) (irradiation source: UVA-340 nm fluorescent light; irradiance: $0,68 \text{ W/m}^2$; chamber temperature: 60°C) with no relative humidity and no condensation cycles. The UV resistance was analyzed by evaluating color and chemical changes on the wood surfaces at regular interval (50h) of exposure.

A spectro-colorimeter (Hunter lab – Lab scan XE model) was used to estimate color changes using CIELab color co-ordinates. Changes in lightness (ΔL^*), redness (Δa^*) and yellowness (Δb^*) were measured on each sample. Total color change ΔE^* were evaluated using equation (2),

$$\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2} \quad (2)$$

FTIR - attenuated total reflectance technique was used to record spectra from wood surfaces using a FTIR spectrometer (Bruker model Tensor 27). Spectra were measured at a spectral resolution of 4 cm^{-1} with 64 scans/measurement.

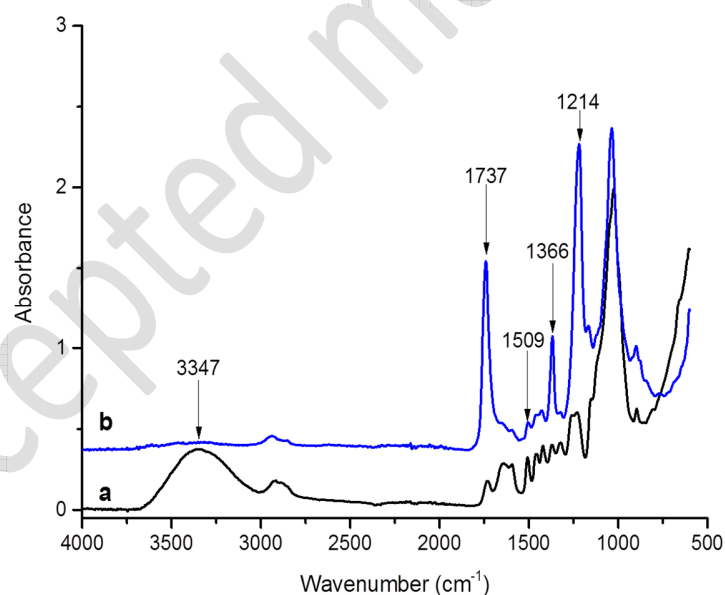
Contact angle of water droplet on unmodified and modified wood surface was measured using a contact angle analyzer by tangent fitting mode (Phoenix 300 Plus model and Surface Electro Optics make having LED light source with accuracy of $\pm 0,1^\circ$).

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RESULTS AND DISCUSSION

100 Acetylation of wood with acetic anhydride:

101 Acetylation of wood resulted in an average WPG of $20,5 \pm 1,2$. Acetylated wood was
102 characterised using FTIR spectroscopy (Fig. 1). Significant reduction in the absorbance of band at
103 3347 cm^{-1} (O–H stretching) and increased absorbance of band at 1737 cm^{-1} (C=O stretching) and
104 1214 cm^{-1} (C–O stretching) indicates of esterification of wood. Reduction in available -OH groups
105 due to acetylation makes wood hydrophobic and dimensionally stable. Hygroscopicity of the
106 modified wood surface was ascertained by contact angle measurement. It was found that the
107 contact angle on acetylated wood was 69° in comparison to 44° for unmodified wood (Fig. 2). The
108 hydrophobic nature of modified wood may influence the distribution and adhesion of nanocoating.



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110 **Figure 1:** FTIR spectra of (a) unmodified and (b) acetylated *W. tinctoria* wood.

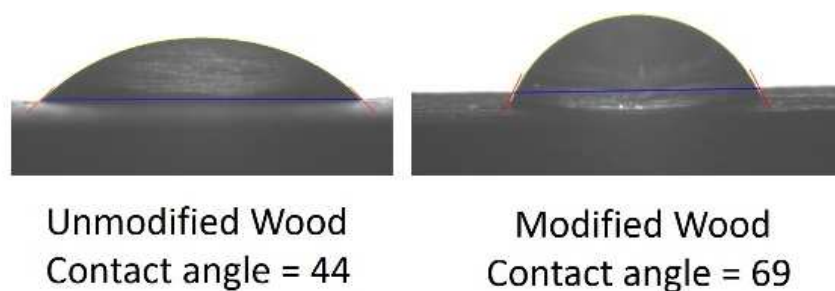


Figure 2: Contact angle of unmodified and acetylated *W. tinctoria* wood.

Characterization of ZnO nano-dispersion:

A stable nanodispersion without any agglomeration was obtained by dispersing ZnO nano particles in PG. No additional surfactant or dispersing agent was used. UV absorption spectra show a broad absorption in UV visible region with $\lambda_{\max} \sim 374$ nm (Fig. 3). The nano dispersion of ZnO was very stable as ascertained using UV Visible spectroscopy (Nair *et al.* 2018). SEM analysis showed uniform distribution of nano particles in PG without any evidence of agglomeration (Fig. 3).

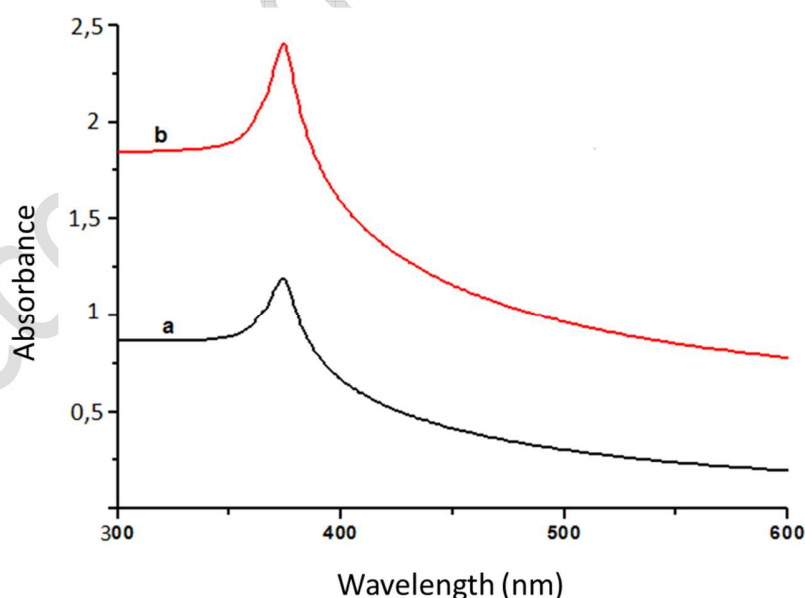


Figure 3: Absorption spectra of (a) 1 % and (b) 2 % ZnO nanodispersions in PG.

Photo-stability of coated wood:

Color changes:

Untreated *W. tinctoria* is a light colored wood with lightness index (L^*) of $79,7 \pm 0,6$. The color of unmodified wood surfaces turned yellow and dark on UV irradiation which is indicated by reduced lightness (L^*) with a corresponding rise in yellowness (b^*). The rate of change was high during initial period of exposure. Most of the color changes were observed within first 50 h of exposure. This trend in color changes is in agreement with several other studies on color changes in light irradiated wood (Tolvaj and Faix 1995; Muller *et al.* 2003; Pandey 2005; Pandey and Vuorinen 2008; Calienno *et al.* 2015; Gonzalez de Cademartori *et al.* 2015; Bonifazi *et al.* 2017; Capobianco *et al.* 2017; Timar *et al.* 2016; Zivkovic *et al.* 2016; Oberhofnerová *et al.* 2017).

UV irradiation of acetylated wood exhibited bleaching, as indicated by lighter color of the irradiated surface. Opposite to unmodified wood, L^* value increased indicating bleaching of acetylated wood on UV exposure. There was only a small change in b^* upon exposure in acetylated wood. Change in lightness (ΔL^*), yellowness (Δb^*) and total color changes (ΔE^*) after 500 h of UV exposure for unmodified and acetylated wood are compared in Fig. 4. As mentioned above, color of unmodified and PG coated specimens deepens/darkened after irradiation with negative ΔL^* values whereas, the color of acetylated specimens turned lighter as indicated by positive ΔL^* values.

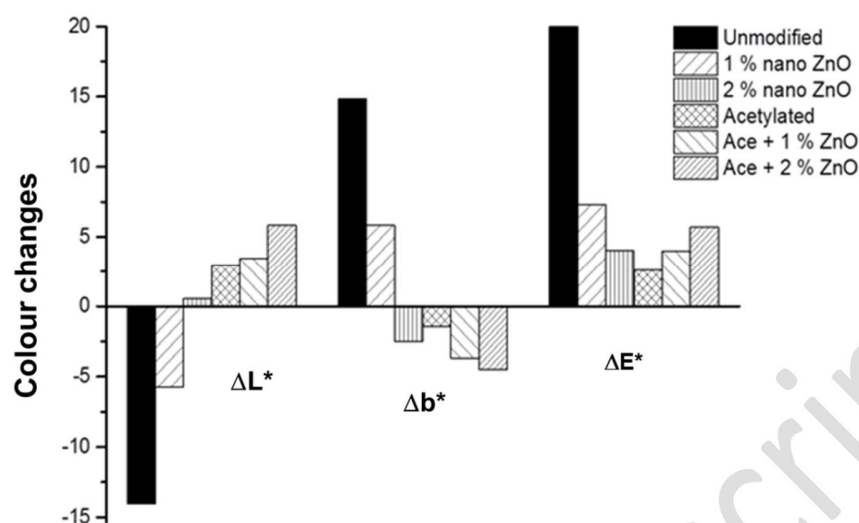


Figure 4: Change in lightness (ΔL^*), change in yellowness (Δb^*) and change in total color (ΔE^*) after 500 h of UV irradiation.

The effectiveness of nano-coating on UV stabilisation of unmodified and modified wood is clearly evident. Though the color darkening (photo-yellowing) was not observed in acetylated wood coated with nano ZnO dispersion, the overall color change (ΔE^*) increased with nano coating application. The total color change in acetylated wood also increased with increase in nanoparticles concentration. This is attributed to the increased lightness of ZnO dispersion coated specimens.

Positive ΔL^* values in acetylated wood showed brightening of wood rather than darkening observed in unmodified wood. Increase in other color co-ordinates *viz.*, Δb^* and redness Δa^* for unmodified wood indicates the changes in yellowness and redness of the specimens due to UV exposure. These color changes of unmodified wood surfaces are generally attributed to the development of conjugated ketones, aldehydes, quinone-like structures involving free radicals mediated depolymerisation and oxidation of lignin (Hon and Chang 1984; Hon 2001; Pandey 2005). In case of acetylated wood, Δb^* values were found to be negative, showing opposite behaviour towards yellowness. These results indicate effectiveness of chemical modification in

restricting light induced darkening /yellowing of wood. Similar observations of photo-bleaching of acetylated wood have been reported earlier (Mitsui 2010; Salla *et al.* 2012; Nagarajappa and Pandey 2016). Acetylation modifies wood structure and decreases photo-induced degradation by blocking the reactive sites (Hon 2001; Kalnins 1984; Temiz *et al.* 2006). These findings support findings of earlier studies (Evans *et al.* 2002; Ohkoshi 2002; Nagarajappa and Pandey 2016; Pandey and Chandrashekar 2006; Jebrane *et al.* 2009).

Color darkening of unmodified wood due to UV irradiations was suppressed by coating of wood surfaces with ZnO nanodispersions. The change in color parameters (L^* , a^* and b^* values) in unmodified wood coated with ZnO nanoparticles were significantly less than uncoated wood. The effectiveness of nano coating increased with increased concentration of nanoparticle. Coating of acetylated wood surfaces with ZnO nanoparticles also reduced light induced color changes. Coating of ZnO nanodispersion on acetylated wood increased its lightness upon exposure to UV light. Similarly, Δb^* values attained negative value upon longer exposure in acetylated wood. However, the extent of change in b^* was very small in acetylated wood. Acetylated wood coated with higher concentration (2 % nanodispersion) exhibited highest bleaching as indicated by increased ΔL^* and reduced Δb^* compared to acetylated wood coated with lower concentrations of nanodispersion. Similarly, variation in redness (Δa^*) was least for acetylated specimens coated with 2 % nano ZnO dispersion. Bleaching observed in acetylated wood due to light irradiation also increased with nano ZnO coating. It can be seen from Fig. 5 that unmodified wood coated with nano dispersion also showed some bleaching effect at higher ZnO concentration. The photo-bleaching of acetylated wood further enhanced with application of nanoparticles coating. This explains enhanced over all color changes in acetylated wood coated with nano ZnO.

Acetylation alone provided significant reduction in total color change (ΔE^*) due to UV degradation in comparison with unmodified wood. Though, nano coating on acetylated wood inhibited yellowing of wood, the anticipated synergistic effect of nano material and acetylation was not seen in ΔE^* . The major contribution in ΔE^* of acetylated wood is from bleaching effect (not color darkening effect). It is important to mention that total color changes (ΔE^*) calculated using eqn. 2 is not an appropriate parameter to compare the UV resistance of chemically modified wood (Nagarajappa and Pandey 2016). This is particularly applicable in the present case as both the color coordinates lightness (ΔL^*) and yellowness (Δb^*) follow contrasting behaviour in unmodified and modified wood and the trend is becoming more intense with nanoparticle coating. Therefore, the variation of individual parameters, particularly L^* and b^* , rather than ΔE^* , is more important to assess the UV stability as has been reported earlier for certain cases (Tolvaj *et al.* 2014, 2015; Nagarajappa and Pandey 2016).

FTIR spectra:

Effect of UV irradiation on FTIR spectra of unmodified and modified wood is shown in Fig. 5. Rapid lignin degradation in modified wood is evidenced from significant reduction in the absorbance of aromatic skeletal vibration ($C=C$) peak at 1505 cm^{-1} and C-H deformation vibration peaks at 1456 cm^{-1} (Pandey 2005; Anderson 1991; Cogulet *et al.* 2016). Peaks at 1505 cm^{-1} and 1456 cm^{-1} almost vanished within 100 h of irradiation. A corresponding increase in absorption peak due to carbonyl groups at 1730 cm^{-1} upon exposure indicates photo-oxidation of lignin. As observed in color measurements, bulk of the changes in FTIR spectra were observed during initial period of exposure. Coating of unmodified wood with ZnO nanodispersion resulted in reduction

in lignin degradation and also restricted increase in carbonyl peak upon light irradiation. This indicates effectiveness of nano coating in preventing lignin degradation and explains reduced color changes in coated wood (Nair *et al.* 2018).

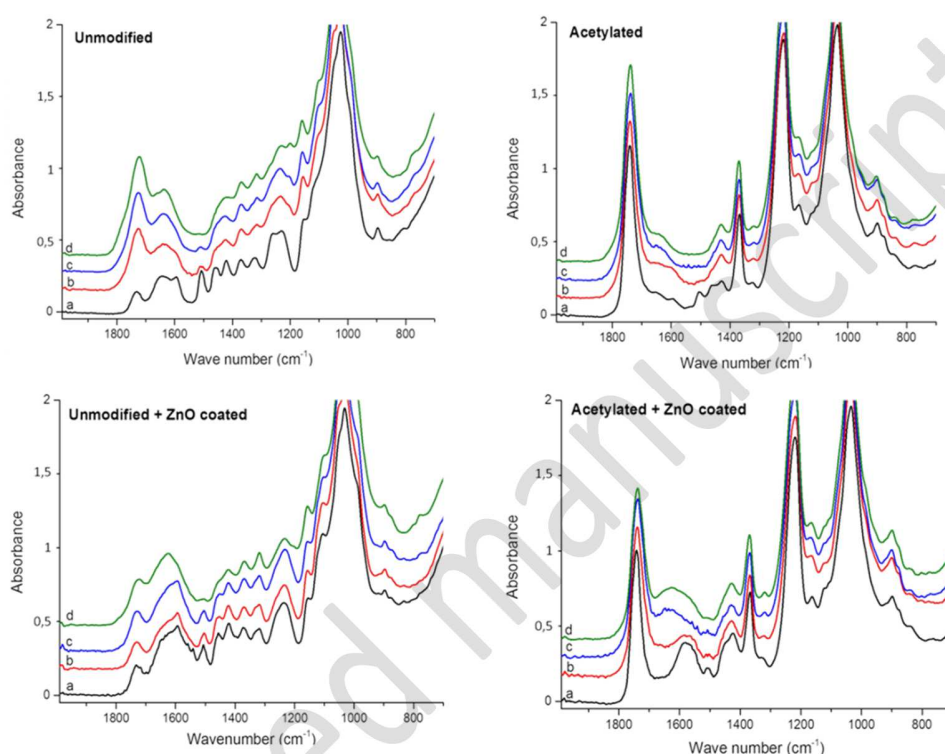


Figure 5: FTIR spectra of unmodified and acetylated wood coated with nano ZnO (2 %) exposed to UV for different durations: (a) unexposed, (b) exposed for 50 h, (c) exposed for 100 h, and (d) exposed for 500 h.

FTIR spectra of acetylated wood also indicated lignin degradation as indicated by reduction in bands at 1505 cm^{-1} , 1456 cm^{-1} . However, the changes in intensities of other peaks were less pronounced in acetylated wood as compared to unmodified specimens. Further, the carbonyl peak at 1740 cm^{-1} remained unaffected in acetylated wood indicating effectiveness of acetylation in reducing UV degradation. Color changes in the UV exposed specimens are result of formation of the colored carbonyl compounds released during the photo-degradation. Acetylated wood

chemically modifies the hydroxyl groups and makes it less accessible to degradation pathway that is initiated by free radicals. The chemical bonding of acetyl groups with wood constituents interferes with light absorption and hence restricts the degradation from UV light.

Coating of unmodified wood with ZnO nanodispersion resulted in reduction in lignin degradation and also restricted increase in carbonyl peak upon light irradiation. This indicates effectiveness of nano coating in preventing lignin degradation and explains reduced color changes in coated wood (Nair *et al.* 2018). FTIR spectra of acetylated wood coated with nanodispersion also indicate some reduction in lignin degradation. Also, intensity of carbonyl peak remained almost unchanged in acetylated wood coated with nano particles. Nanoparticles are known to protect wood from photo-degradation. Coating of ZnO, CeO₂, TiO₂ nanodispersions protected wood significantly from UV degradation with significant reduction in color changes and FTIR (Nair *et al.* 2018). The results of this study indicate that effectiveness of nanodispersion coating in unmodified wood is high. Nano coating improved UV resistance of modified wood also. An enhancement in photo-bleaching of wood coated with ZnO nanoparticle was observed, which increases with increase in ZnO concentration. ZnO, being a good UV absorber, may undergo some bleaching. The photo-bleaching effect observed in chemically modified wood increased with application of nano-coating.

CONCLUSIONS

Acetylation slows down the photo-yellowing of wood surfaces. Application of ZnO nano coating on unmodified and modified wood inhibited photo-discoloration of wood. The apparent higher effectiveness of nanocoating in unmodified wood is due to photo-bleaching effect observed in

acetylated wood. The photo-bleaching effect observed in acetylated wood was further enhanced by application of nano ZnO coating on modified wood surfaces.

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